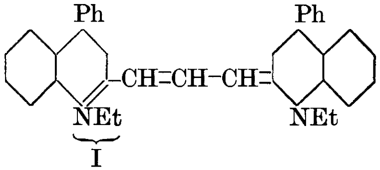
34. *Cyanine Dyes and Related Compounds.*

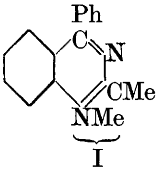
By (Miss) Frances Mary Hamer, Isidor Morris Heilbron, Joseph Henry Reade, and Harold Norman Walls.

Although many classes of cyanine and carbocyanine dyes have been extensively examined during the last two decades and their structures elucidated largely owing to the striking investigations of Mills and Wishart (J., 1920, **117**, 579), Mills and Hamer (*ibid.*, p. 1550), Mills (J., 1922, **121**, 455), König (*Ber.*, 1922, **55**, 3293), Braunholtz and Mills (J., 1923, **123**, 2804), Mills and Odams (J., 1924, **125**, 1913), König (*Ber.*, 1924, **57**, 685), König and Meier (*J. pr. Chem.*, 1925, **109**, 324), Hamer (J., 1927, 2796; 1928, 206, 1472, 3160; 1929, 2598), Fisher and Hamer (J., 1930, 2502), and Hamer and Kelly (J., 1931, 777), the relationship between chemical constitution and photographic properties still remains largely obscure. In the present paper an attempt has been made to gain some further insight into the problem by the preparation of new compounds similar in character to known photographically active dyes.

Carbocyanines.—We have in the first instance taken as standard the important photographic sensitiser pinacyanol (Mills and Hamer, *loc. cit.*; König, *loc. cit.*) and modified the quinoline nuclei in this dye by employing in place of quinaldine itself 4-phenylquinaldine, the *ethiodide* of which is readily convertible into 4 : 4'-*diphenyl*-1 : 1'-*diethyl*-2 : 2'-*carbocyanine iodide* (I).

(I.)





(II.)

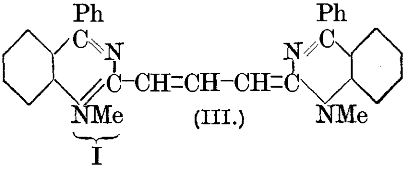
The dye confers a certain extra-sensitivity on a photographic plate, the maximum effect being at 665 mμ, but the amount of the sensitisation is far less than with pinacyanol.

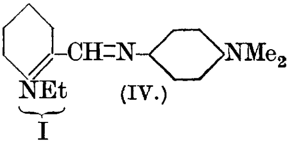
The corresponding 4 : 4'-*diphenyl*-1 : 1'-*dimethyl*-2 : 2'-*carbocyanine iodide*, on the other hand, imparts no extra-sensitivity to a photographic plate, but exerts a very slight desensitising effect, which is decreased by both sodium sulphite and carbonate; its principal absorption band shows a maximum at 625 mμ and there is also a secondary band with head at 575 mμ.

It is thus evident that (*a*) the presence of the 4 : 4'-phenyl radicals in the quinoline nuclei markedly decreases the sensitising properties of the dye, and (*b*) methyl groups in the 1 : 1′-positions are less favourable to the development of photographic sensitisation than ethyl radicals. The latter observation is in agreement with the results obtained by Mills and Pope (*Phot. J.*, 1920, **60**, 253), who noted that the methyl analogue of pinacyanol was a comparatively poor sensitiser (compare also Hamer, J., 1929, 2598).

The striking difference in photographic behaviour occasioned by replacement of methyl by ethyl groups has led us to examine 1 : 1′-*di*iso*propyl*-2 : 2′-*carbocyanine iodide*. This salt proves to be as powerful a panchromatic sensitiser as pinacyanol itself, with action actually extending further into the red region. The chief absorption maximum is at 605 mμ and there is a weaker one at 560 mμ.

Our attention was next turned to the preparation of sensitising dyes containing quinazoline nuclei. Attempts to prepare dyes of this type have been recorded by Bogert and Clark (*J. Amer. Chem. Soc.*, 1924, **46**, 1294), who found, however, that the simple quinazolines failed to yield quaternary alkyl salts. On the other hand, although such salts could be obtained from the 4-quinazolones (Bogert and Geiger, *ibid.*, 1912, **34**, 683), they failed to yield cyanine dyes under the experimental conditions employed (Bogert and Clark, *loc. cit.*). We have now succeeded in preparing 4-*phenyl*-2-*methylquinazoline methiodide* (II) by the action of phenylmagnesium bromide upon 1 : 2-dimethyl-4-quinazolone (Heilbron, Kitchen, Parkes, and Sutton, J., 1925, **127**, 2167) and find that this salt readily condenses with ethyl orthoformate according to Hamer's method (J., 1927, 2796), giving 4 : 4′-*diphenyl*-1 : 1′-*dimethylquinazocarbocyanine iodide* (III).


(III.)


(IV.)

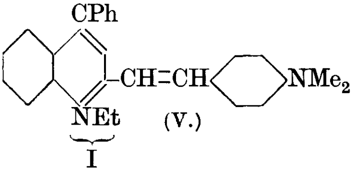
The dye (III) possesses two approximately equal and scarcely separable absorption bands with maxima at 630 mμ and 590 mμ respectively, and differs in this respect from a typical 2 : 2′-carbocyanine derived from a quinaldinium salt, where the band nearer to the red end of the spectrum is normally more powerful. The substance gives clean plates, does not affect the latent image, and is practically devoid of either sensitising or desensitising photographic properties. In this respect it resembles 4 : 4′-diphenyl-

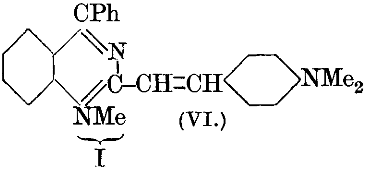
1 : 1′-dimethyl-2 : 2′-carbocyanine iodide, and shows that the quinazoline nuclei exert no outstanding photographic action.

The replacement of a cyclic methine group by nitrogen thus produces a wholly different effect from that caused by similar replacement in the conjugated aliphatic methine chain, for, as shown by Bloch and Hamer (*Phot. J.*, 1930, **70**, 374), whereas the *p*-dimethylaminoanil of pyridine-2-aldehyde ethiodide (IV) has strong desensitising capacity, 2-*p*-dimethylaminostyrylpyridine ethiodide is a powerful photographic sensitiser (Mills and Pope, J., 1922, **121**, 946. For other instances, see Smith, J., 1923, **123**, 2288; Hamer, J., 1924, **125**, 1348; *Phot. J.*, 1929, **69**, 409).

Styryl Derivatives.—There are in the literature several references to the photographic properties of styryl derivatives of quaternary salts, in which a nitrogen atom forms one member of a heterocyclic nucleus. The photographic behaviour varies, however, according to the other substituents present. Thus, on the one hand, the photographic sensitising action of such compounds has been recorded (Barbier, *Bull. Soc. chim.*, 1920, **27**, 427; Mills and Smith, J., 1922, **121**, 2724; Smith, *loc. cit.*; Hamer, J., 1924, **125**, 1348; Bloch and Hamer, *loc. cit.*), whilst, on the other hand, other compounds of this type, such as 6-ethoxy-2-styrylquinoline ethiodide, desensitise (Farbw. vorm. Meister, Lucius, and Brüning, G.P. 396,402; I. G. Farbenind. A.-G., B.P. 262,816; Hamer, *Phot. J.*, 1929, **69**, 409).

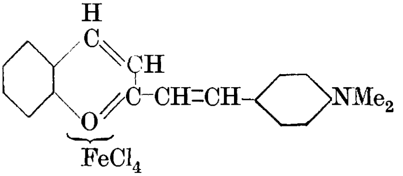
An examination of the styryl derivatives of the quaternary salts described above has now been made and here again definite effects due to the 4-phenyl group become apparent. Thus, whereas 2-*p*-dimethylaminostyrylquinoline ethiodide possesses sensitising action (Hamer, J., 1924, **125**, 1348), this is much weaker in the case of *4-phenyl-2-*p*-dimethylaminostyrylquinoline ethiodide* (V), while the *methiodide* (which has, like the preceding compound, a broad absorption band with a crest at 530 mμ) exerts considerable desensitising power and causes no destruction of the latent image. Replacement of the dimethylamino-radical by hydroxyl also gives interesting results, for *4-phenyl-2-*p*-hydroxystyrylquinoline methiodide*, which has a broad absorption band with a maximum at 430 mμ, has a desensitising capacity equal to that of safranine for fast non-colour-sensitive plates, but is not so good for panchromatic plates. The plates are free from chemical veil and there is no destruction of the latent image. *4-Phenyl-2-*p*-hydroxystyrylquinoline ethiodide* and *4-phenyl-2-*p*-methoxystyrylquinoline ethiodide* do not sensitise; in both cases, the absorption band lies in the blue region and extends to about 500 mμ. *4-Phenyl-2-*p*-dimethylaminostyrylquinazoline methiodide* (VI) also has been prepared; it possesses one broad absorption band with a maximum at 540 mμ and produces slight desensitisation.


(V.)

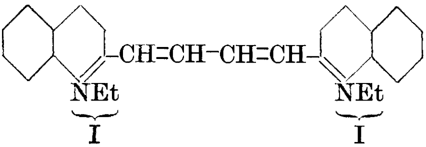

(VI.)

Owing to the close structural analogy which exists between styryl derivatives of quinolinium salts and the corresponding derivatives of benzopyrylium salts, twelve members of the latter class have been tested for photographic behaviour. The striking result emerges that there is no parallelism whatever. Only in two instances was there even a trace of sensitisation; (1) 7-hydroxy-2-*p*-dimethylaminostyryl-4-methylbenzopyrylium chloride (Heilbron, Walker, and Buck, J., 1925, **127**, 690), which absorbs in the green with a badly-defined maximum at 580 mμ, shows sensitisation at 640 mμ, and (2) 3 : 6-dihydroxy-9-*p*-dimethylaminostyrylxanthylium chloride (Atkinson and Heilbron, J., 1926, 676), which has an absorption maximum at 440 mμ, produces a very feeble extension of the normal sensitivity. It is well known that sensitisation and desensitisation may occur simultaneously, but there is no desensitisation with these three dyes nor with the following: (3) 4′-hydroxy-3′-methoxy-2-styrylbenzopyrylium chloride (Buck and Heilbron, J., 1922, **121**, 1198, (4) 5 : 7-dimethoxy-2-phenyl-4-*p*-dimethylaminostyrylbenzopyrylium chloride (Walker and Heilbron, J., 1925, **127**, 685), which absorbs in the deep red, (5) 5 : 7-dihydroxy-2-phenyl-4-*p*-dimethylaminostyrylbenzopyrylium ferrichloride (*idem, ibid.*), which has a broad absorption band with its crest at 550 mμ and produces dense patchy fog on a photographic plate, (6) 7-hydroxy-2-*p*-methoxystyryl-4-*p*-dimethylaminostyrylbenzopyrylium chloride (Heilbron, Walker, and Buck, *loc. cit.*), which shows much absorption between 460 and 640 mμ but with no definite maximum, and (7) 3-*p*-dimethylaminostyryl-β-naphthapyrylium perchlorate (Dickinson and Heilbron, J., 1927, 14), which has a broad ill-defined absorption band with its maximum at 450 mμ and attacks the latent photographic image and produces foggy streaks and patches. There is slight desensitisation in the case of (8) 2-*p*-methoxystyrylbenzopyrylium chloride (Buck and Heilbron, *loc. cit.*), (9) 3-styryl-β-naphthapyrylium chloride (Dickinson and Heilbron, *loc. cit.*), which absorbs from the ultra-violet up to 440 mμ, (10) 3-(β-2′-hydroxy-1′-naphthylvinyl)-β-naphthapyrylium chloride (*idem, ibid.*), and (11) 4-*phenyl*-2 : 6-pp′-*tetramethyldiaminodistyryl*-

pyrylium ferrichloride (see experimental portion), which has one broad absorption band with its maximum at 550 mμ and a narrower one with its maximum at 435 mμ. The most interesting member of the series (12) is 2-*p*-dimethylaminostyrylbenzopyrylium ferrichloride (VII) (Buck and Heilbron, J., 1923, **123**, 1395). It is characterised by an ill-defined absorption maximum at 635 mμ and possesses more powerful desensitising properties than safranine itself, whether with colour-sensitive or with non-colour-sensitive plates. It is well known that ferric salts exert an apparent desensitisation, which is, in reality, destruction of the latent image (Steigmann, *Phot. Ind.*, 1922, 71; 1925, 490; Ross, *Brit. J. Phot.*, 1925, **72**, 19; Bullock, *ibid.*, 1927, **74**, 590); there is, in the case of this double salt, no evidence that its desensitising action is dependent upon the iron content. Unfortunately none of these benzopyrylium salts is of practical value, as the desensitisation is destroyed by sodium carbonate and sodium sulphite.



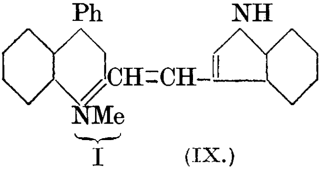
(VII).



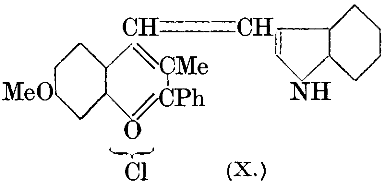
(VIII.)

2 : 2′-*Divinylene Salts.*—Dependent upon the fact that in the cyanine group the methine chain comprises an uneven number of carbon atoms, the molecule exhibits a kind of virtual tautomerism (Mills and Braunholtz, J., 1922, **121**, 1489). In order to obtain direct evidence of the influence of this effect upon both colour and photographic properties, we have now prepared a series of symmetrical 2 : 2′-divinylene salts and obtained new types which differ from the true cyanines more than they resemble them. 2 : 2′-*Divinylenediquinoline* 1 : 1′-*diethiodide* (VIII), which is readily formed by heating quinaldine ethiodide with glyoxal in dry pyridine, is a red dye having one broad absorption band with its head at 510 mμ, and is wholly devoid of sensitising action. The same applies to 4 : 4′-*diphenyl*-2 : 2′-*divinylenediquinoline* 1 : 1′-*diethiodide* and 4 : 4′-*diphenyl*-2 : 2′-*divinylenequinazoline* 1 : 1′-*dimethiodide*, both of which actually slightly decrease the normal sensitivity of a photographic plate.

Further illustrations of the effect of restraining the oscillatory movement between the heterocyclic nuclei upon visible colour have been obtained by examining the dyes formed by condensing 4-phenylquinaldine methiodide and 4-phenyl-2-methylquinazoline methiodide with indole-3-aldehyde. Whereas both the carbocyanines containing these heterocyclic nuclei dye natural silk and wool bright blue shades, 4-*phenyl*-2-3′-*indolylvinylquinoline methiodide* (IX) and its quinazoline analogue, in both of which the unsaturated carbon chain linking the nitrogen atoms is similar to that in the carbocyanine group, only dye natural silk and wool brick-red shades.



(IX.)



(X.)

The powerful chromogenic effect of the benzopyrylium nucleus is very clearly shown in this series, for the dye (X), obtained by condensing 7-methoxy-2-phenyl-3 : 4-dimethylbenzopyrylium chloride (Heilbron and Zaki, J., 1926, 1902) and indole-3-aldehyde, gives bright purplish-blue shades on wool. Heilbron and Zaki (*loc. cit.*) considered that the parent benzopyrylium salt was 7-methoxy-4-phenyl-2 : 3-dimethylbenzopyrylium chloride, having prepared it by the action of the Grignard reagent on what they considered was 7-methoxy-2 : 3-dimethylchromone. It has recently been shown, however, by Canter, Curd, and Robertson (J., 1931, 1255), and confirmed in this laboratory, that the latter compound, which was prepared by the Simonis method from resorcinol and ethyl methylacetoacetate (*Ber.*, 1914, **47**, 2229), is actually the isomeric 7-methoxy-2-phenyl-3 : 4-dimethylcoumarin.

EXPERIMENTAL.

4-*Phenyl*-2-*methylquinazoline Methiodide* (II).—A solution of 1 : 2-dimethyl-4-quinazolone (8 g.) (Heilbron, Kitchen, Parkes, and Sutton, *loc. cit.*) in dry anisole (180 c.c.) was slowly treated with phenylmagnesium bromide (from bromobenzene, 17·5 g., in 100 c.c. of ether); a yellow precipitate formed which gradually redissolved. The mixture was heated for 3 hours on a steam-bath and decomposed with cold dilute hydrochloric acid. The acid layer was separated and rendered alkaline with dilute aqueous ammonia, and the brown-red colour base was removed, dissolved in alcohol, and heated for $\frac{1}{2}$ hour with excess of hydriodic acid. The resultant greenish-yellow solution was poured into hot water and concentrated; 4-*phenyl-2-methylquinazoline methiodide* separated in canary-yellow needles, m. p. 208° (decomp.), readily soluble in water and alcohol (Found: C, 53·1; H, 4·5; N, 7·7. $C_{16}H_{15}N_2I$ requires C, 53·0; H, 4·1; N, 7·7%).

4-*Phenyl*-2-p-*dimethylaminostyrylquinazoline methiodide* (VI) was prepared by heating an alcoholic solution of the above salt (2 g.) and *p*-dimethylaminobenzaldehyde (0·9 g.) under reflux for 4 hours in presence of a few drops of piperidine. The *styryl* salt separated from the cold solution in purple feathery needles with a green metallic reflex; m. p. 202° (decomp.) (Found: N, 8·3. $C_{25}H_{24}N_3I$ requires N, 8·5%).

4-*Phenyl*-2-o-*hydroxystyrylquinazoline methiodide*, prepared similarly, crystallised from alcohol in fine orange needles, m. p. 182° (decomp.) (Found: N, 5·8. $C_{23}H_{19}ON_2I$ requires N, 6·0%).

4 : 4′-*Diphenyl*-1 : 1′-*dimethylquinazocarbocyanine Iodide* (III).—A solution of 4-phenyl-2-methylquinazoline methiodide (2 g.) and ethyl orthoformate (1·6 g.) in pyridine (40 c.c.) was heated under reflux for 5 hours, and the resultant greenish-blue solution concentrated; the *salt* then separated in greenish-red metallic lustrous needles, m. p. 270°, sparingly soluble in water and alcohol, more readily in pyridine. It dyes wool and silk a bright blue shade (Found: N, 9·1. $C_{33}H_{27}N_4I$ requires N, 9·2%).

4 : 4′-*Diphenyl*-2 : 2′-*divinylenediquinazoline* 1 : 1′-*Dimethiodide.*—This *salt* was prepared by refluxing a solution of 4-phenyl-2-methylquinazoline methiodide (4 g.) with glyoxal (0·8 g.) in pyridine (15 c.c.) for ½ hour. It slowly separated on cooling from the bright red solution in dull brownish-red needles, m. p. 205° (decomp.), sparingly soluble in water but moderately easily soluble in alcohol and acetone. It dyes wool and silk dull red shades (Found: N, 7·2. $C_{34}H_{28}N_4I_2$ requires N, 7·5%).

4-*Phenyl*-2-p-*dimethylaminostyrylquinoline Ethiodide* (V).—4-Phenylquinaldine (Beyer, *Ber.*, 1887, **20**, 1767) was converted into the ethiodide (yellow needles, m. p. 200—201°) by refluxing with ethyl iodide in benzene solution. A solution of this salt (3 g.) and *p*-dimethylaminobenzaldehyde (1·2 g.) in alcohol (50 c.c.) was kept over-night at 60° in presence of one drop of piperidine. The intense bluish-red solution on cooling set to a solid mass. The pure *salt* crystallised from alcohol in deep purple needles with a green metallic reflex (Found: N, 5·5. $C_{27}H_{27}N_2I$ requires N, 5·5%). The corresponding *methiodide*, m. p. 227° (decomp.), formed similarly from 4-phenylquinaldine methiodide (m. p. 205°), is similar in all respects (Found: N, 5·8. $C_{26}H_{25}N_2I$ requires N, 5·7%).

4-*Phenyl*-2-p-*hydroxystyrylquinoline methiodide*, prepared in an analogous manner from 4-phenylquinaldine methiodide and *p*-hydroxybenzaldehyde, forms orange-brown needles readily soluble in hot water to give a deep yellow solution which changes to blue-red on addition of alkali (Found : N, 2·8. $C_{24}H_{20}ONI$ requires N, 3·0%). The *ethiodide*, m. p. 220° (decomp.), is similar in all respects (Found : N, 3·2. $C_{25}H_{22}ONI$ requires N, 2·9%).

4-*Phenyl*-2-p-*methoxystyrylquinoline ethiodide*, prepared from 4-phenylquinaldine ethiodide, separates from alcohol in orange-brown needles, m. p. 247°. The salt is sparingly soluble in alcohol, acetone, and hot water to give bright yellow solutions which dye tannin-mordanted cotton or silk bright yellow shades which are unaffected by dilute mineral acids or alkali (Found : C, 63·0 ; H, 5·0. $C_{26}H_{24}ONI$ requires C, 63·3 ; H, 4·9%).

4 : 4′-*Diphenyl*-1 : 1′-*dimethyl*-2 : 2′-*carbocyanine Iodide*.—A solution of 4-phenylquinaldine methiodide (4·3 g.) in acetic anhydride (90 c.c.) was maintained together with ethyl orthoformate (3 g.) just below its boiling point for 20 minutes; the whole rapidly attained a bright green colour and fine needles quickly separated. The pure *salt* crystallised from alcohol in brownish-green felted needles with a gold reflex, and is sparingly soluble in water and alcohol. The reaction proceeds less satisfactorily when pyridine is employed in place of acetic anhydride as solvent (Found : N, 4·9. $C_{35}H_{29}N_2I$ requires N, 4·6%).

The corresponding 4 : 4′-*diphenyl*-1 : 1′-*diethyl*-2 : 2′-*carbocyanine iodide* (I) is similar in appearance but is somewhat more soluble in alcohol (Found : N, 4·5. $C_{37}H_{33}N_2I$ requires N, 4·4%).

4 : 4′-*Diphenyl*-2 : 2′-*divinylenediquinoline* 1 : 1′-*Dimethiodide*.—A solution of 4-phenylquinaldine methiodide (3·5 g.) in dry pyridine was boiled for 2 hours under reflux with glyoxal (0·6 g.). The solution quickly acquired an intense purple-red colour, and the *salt* separated on cooling. It crystallised from pyridine in dark greenish-brown metallic lustrous needles difficultly soluble in water, more soluble in alcohol, in which it forms an intense bluish-red solution. It dyes wool and silk full deep red shades (Found : N, 3·8. $C_{36}H_{30}N_2I_2$ requires N, 3·8%).

The corresponding *diethiodide* forms deep red plates with a green metallic reflex (Found : N, 3·8. $C_{38}H_{34}N_2I_2$ requires N, 3·6%).

2 : 2′-*Divinylenediquinoline* 1 : 1′-*diethiodide* (VIII) was prepared in an analogous manner from quinaldine ethiodide. The salt crystallised from alcohol in minute, dark red plates. Attempts to prepare this compound in acetic anhydride solution were unsuccessful (Found : N, 4·7. $C_{26}H_{26}N_2I_2$ requires N, 4·5%).

Quinaldine iso*Propiodide*.—A solution of quinaldine (10 g.) and *iso*propyl iodide (10 g.) in dry benzene was refluxed on the water-bath for several days, the *salt* being gradually deposited on the sides of the flask. It crystallised from absolute alcohol (charcoal) in cream-coloured needles, m. p. 163—165° (decomp.) (Found: N, 4·7. $C_{31}H_{16}NI$ requires N, 4·4%).

1 : 1′-*Diisopropyl*-2 : 2′-*carbocyanine Iodide*.—Quinaldine *iso*-propiodide (4 g.) in acetic anhydride (25 c.c.) was treated with ethyl orthoformate (4 c.c.), which was added during 10 minutes, the solution being maintained just below its boiling point. After a further ½ hour, the solution was allowed to cool; the salt then separated in bluish-green needles and was recrystallised from acetone (Found: N, 5·7. $C_{27}H_{29}NI$ requires N, 5·5%).

4-*Phenyl*-2-3′-*indolylvinylquinoline Methiodide* (IX).—4-Phenyl-quinaldine methiodide (3·5 g.) and indole-3-aldehyde (1·5 g.) were dissolved in alcohol (20 c.c.) together with 2 drops of piperidine and the solution was gently boiled under reflux for 2 hours; the *salt*, which was gradually deposited, crystallised from alcohol in red-brown crystals, m. p. 252° (decomp.) (Found: N, 5·8. $C_{26}H_{21}N_2I$ requires N, 5·7%).

4-*Phenyl*-2-3′-*indolylvinylquinazoline methiodide* was prepared in an analogous manner. It separated from alcohol in reddish-brown needles, m. p. 238° (decomp.), and dissolved in water to a brick-red solution (Found: N, 8·7. $C_{25}H_{20}N_3I$ requires N, 8·6%).

7-*Methoxy*-2-*phenyl*-3-*methyl*-4-3′-*indolylvinylbenzopyrylium Chloride* (X).—A solution of 7-methoxy-2-phenyl-3 : 4-dimethylbenzopyrylium chloride (3 g.) (Heilbron and Zaki, *loc. cit.*) and indole-3-aldehyde (2 g.) in alcohol (200 c.c.) was gently boiled on a water-bath for 2 hours. The *salt*, which separated from the cold, deep purple solution, was crystallised from alcohol, forming bluish metallic needles readily soluble in alcohol, sparingly soluble in water (Found: N, 3·7. $C_{28}H_{22}O_2NCl$ requires N, 3·2%).

4-*Phenyl*-2 : 6-pp′-*tetramethyldiaminodistyrylpyrylium Ferrichloride*.—4-Phenyl-2 : 6-dimethylpyrylium perchlorate (8 g.) (Baeyer and Piccard, *Annalen*, 1911, **384**, 208) was converted into the base by shaking with ether and dilute sodium carbonate solution. The dark red ethereal layer (300 c.c.) was separated, dried over anhydrous sodium sulphate, and treated with dry hydrogen chloride until no further red oil separated. After decantation of the ether, the oil was dissolved in absolute alcohol (30 c.c.), *p*-dimethylaminobenzaldehyde added, and the whole gently heated; the colour changed from deep red to blue-green (10 mins.). Treatment of the hot solution with hydrated ferric chloride precipitated the double salt as an oil which solidified on cooling; it was purified by crystallisation from acetone. The *ferrichloride* forms deep purple needles with a bronze reflex; it is readily soluble in acetone to a blue-green solution which on dilution with water attains a pure green colour (Found : N, 4·3. $C_{31}H_{31}ON_2Cl_4Fe$ requires N, 4·3%).

The absorption spectra recorded above are, in all cases, those of spirit solutions. To test for sensitising properties, gelatino-bromide photographic plates were bathed in dilute aqueous-alcoholic solutions of the dyes before exposure in the spectrograph.

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